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# Structural and magnetic properties of $Mn_3O_4$ films grown on MgO(0 0 1) substrates by plasma-assisted MBE

L.W. Guo[a,c], D.L. Peng[a], H. Makino[a], K. Inaba[b], H.J. Ko[a], K. Sumiyama[a], T. Yao[a,*]

[a]*Institute for Materials Research, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980, Japan*
[b]*X-Ray Research Laboratory, Rigaku Corporation, Tokyo, Japan*
[c]*Institute of Physics, Chinese Academy of Sciences, Beijing 100080, China*

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**Abstract**

$Mn_3O_4$ thin films with distorted spinel structure are grown on MgO(0 0 1) substrates by plasma-assisted molecular beam epitaxy (MBE). The films are (0 0 1) oriented and the lattice parameters are $a = b \approx 5.72$ Å, and $c \approx 9.5$ Å, with $c/a = 1.66$ slightly larger than the ratio of 1.64 for bulk single-crystal samples, if a body-center tetragonal unit cell is adopted for $Mn_3O_4$. It is found that the Curie temperature $T_{CF}$ of the $Mn_3O_4$ film is 46 K higher than ($T_{CB} = 42$ K) for bulk single-crystal samples. The spontaneous magnetization reaches 1.73 $\mu_B$/molecule which is in between the reported results of 1.56 $\mu_B$/molecule for polycrystalline and 1.85 $\mu_B$/molecule for single-crystal sample. The temperature dependence of the inverse magnetic susceptibility in the paramagnetic range agrees well with the Curie–Weiss formula. The induced effective magnetic moment for Mn ion is about 3.59 $\mu_B$, which is small compared with the 5.24 $\mu_B$/magnetic atom calculated based on electronic spins only. 

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## 1. Introduction

Bulk $Mn_3O_4$ crystals as one of the stable phases of Mn oxides have been studied well from both theoretical and experimental point of view [1–7]. $Mn_3O_4$ is known to crystallize in the spinel structure with tetragonal distortion elongated along the *c*-axis, with lattice parameters $a = b = 5.76$ Å, $c = 9.46$ Å. Manganese ions are placed on the octahedral B-site ($Mn^{3+}$) and tetrahedral A-site ($Mn^{2+}$), corresponding to a *normal* spinel structure. Ferrimagnetic long-range order had been found with lower spontaneous magnetization than that predicted by the simple Néel model in various samples with spinel structure. Most of the studies on

* Corresponding author. Tel.: + 0081-022-215-3067; fax: + 0081-022-215-2073.
*E-mail address:* yao@imr.tohoku.ac.jp (T. Yao).

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magnetic properties of $Mn_3O_4$ have been, however, performed on the bulk samples [1,4].

With the progress of thin-film technology, various high-quality single-crystal films, such as semiconductors, superconductors and magnetic films, have shown many unique properties different from bulk single crystals due to strain, structural defects, interface, and morphology effects. Compared with magnetic properties of $Mn_3O_4$ bulk single crystals, the understanding of film properties is still poor. Although there were few reports on thin films grown by chemical vapor deposition (CVD) [8,9], there has been no information about their magnetic properties. Consequently, in the present work, molecular beam epitaxy (MBE) has been adopted to grow single-crystal $Mn_3O_4$ thin films to study their magnetization and phase transition temperature, as well as the effects of interface and crystal quality on magnetization.

## 2. Experimental

$Mn_3O_4$ single-crystal films were grown on MgO(0 0 1) substrates by plasma-assisted MBE with a typical background pressure of $8\times10^{-10}$ Torr. Elemental manganese was used as Mn source, which was evaporated by a conventional Knudsen cell (K-cell) at 680–820°C. Atomic oxygen was produced by a microwave plasma source with an excited radiation frequency (RF) of 13.56 MHz and a maximum output power of 400 W. Mn oxide films were grown at substrate temperature around 550–750°C. The $O_2$ pressure during growth in the chamber was kept at $4\times10^{-5}$ Torr.

The deposited films are in the thickness range of 300 nm to 1.47 μm as determined by Alpha-step measurement. Their crystal quality and surface morphology were characterized by X-ray diffraction (XRD) and atomic force microscope (AFM) [10]. Magnetization properties of the films were measured using a superconducting quantum interference device (SQUID) magnetometer capable of operating in the temperature range 5–300 K, and magnetic field range 0–50 000 Oe applied parallel to the plane of the films.

## 3. Results and discussion

### 3.1. Structure of the $Mn_3O_4$ film

Since the deposited $Mn_3O_4$ single-crystal films are in the thickness range of 300 nm to 1.47 μm which is much larger than the critical thickness of $Mn_3O_4$ on MgO with 3.3% misfit, they are nearly relaxed to its bulk lattice parameters. Meanwhile, they exhibit slight distortion from the bulk parameters and ideal square symmetry in the growing plane as characterized by XRD analysis. The detailed XRD analysis [10] suggested that the films are (0 0 1) oriented, and the [1 1 0] axis is parallel to the [1 0 0] axis of the MgO substrate, if a body-centered tetragonal unit cell is assumed. The lattice constants of the films are $a=b\approx5.72$ Å and $c\approx9.5$ Å which gives a ratio $c/a=1.66$ larger than the value 1.64 for the bulk structure. It was found that the quality of the films has a close correlation with the film thickness and the quality of MgO substrate. The full-width at half-maximum (FWHM) of the (0 0 4) diffraction peak decreased from 0.4 to 0.17° with increasing the film thickness from 300 nm to 1 μm. The wide FWHM of the films

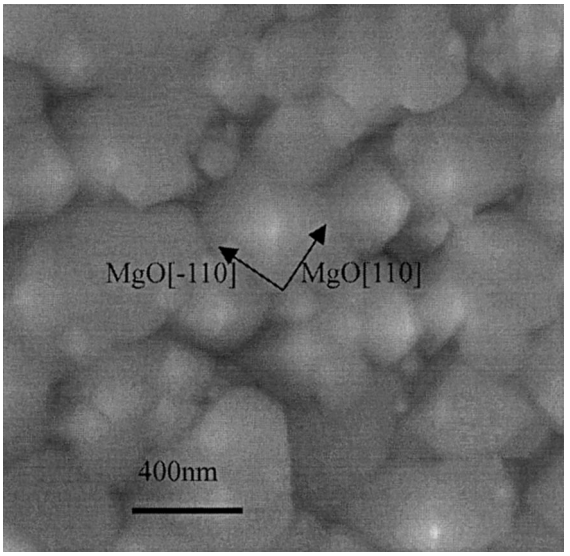


Fig. 1. AFM image of an $Mn_3O_4$ film. The base edges of the pyramid-hillocks are parallel to the MgO[1 1 0] (or [ $\bar{1}$ 1 0]) direction.

are attributed to the high-angle-oriented MgO substrates. It is inferred that the thicker the film is, the better its quality is. A detailed X-ray analysis has been given in Ref. [10]. For all our films, their surfaces are characterized as perfect crystallized pyramid-hillocks composed of facets $\{1\,0\,n\}$ where $n$ is an integer around 15 [10]. Fig. 1 shows the typical morphology of an $Mn_3O_4$ film measured by AFM, the base edges of the pyramid-hillocks are parallel to the [1 1 0] direction of the MgO substrate.

### 3.2. Dependence of magnetization on magnetic field

The $Mn_3O_4$ films show ferrimagnetic long-range order when the temperature is lower than the Curie temperature ($T_C$) owing to the exchange interaction of Mn atoms, which is similar to the behavior of bulk samples. Since there is large shape anisotropy for $Mn_3O_4$ film samples, the magnetization measurement was performed in the (0 0 1) plane. Fig. 2 shows hysteresis loops at 5 K under an applied magnetic field along the [1 0 0] and [1 1 0] directions. It was found that the easy axis of magnetization in the (0 0 1) plane is along the [1 0 0] or [0 1 0] direction of the film with a coercive force of about 3500 Oe for magnetization reversal for a thicker film (1.47 μm), which is larger than the value of 2800 Oe for a bulk single-crystal sample [1]. Comparing with [1 0 0] axis, the [1 1 0] axis is slightly harder than the [1 0 0] axis with a coercive force of about 2500 Oe. From the hysteresis loop for the field along the [1 0 0] direction in Fig. 2, the spontaneous magnetization of the film is estimated to be 1.73 $\mu_B$/molecule by extrapolation to zero field from the high-field asymptote.

It has been reported that the spontaneous magnetization is 1.85 $\mu_B$/molecule [1] for $Mn_3O_4$ single crystal and 1.56 $\mu_B$/molecule [4] for polycrystalline samples. Clearly, the spontaneous magnetization of the film is in between these values. The smaller value of the polycrystalline sample is because of the anisotropy effect owing to disorder in the crystal orientation, which can be avoided in single-crystal sample by applying an external field along an easy magnetization axis. However, all these reported results are still less than the 3 $\mu_B$/molecule predicted by the simple Néel model of ferrimagnetism. A reasonable explanation has

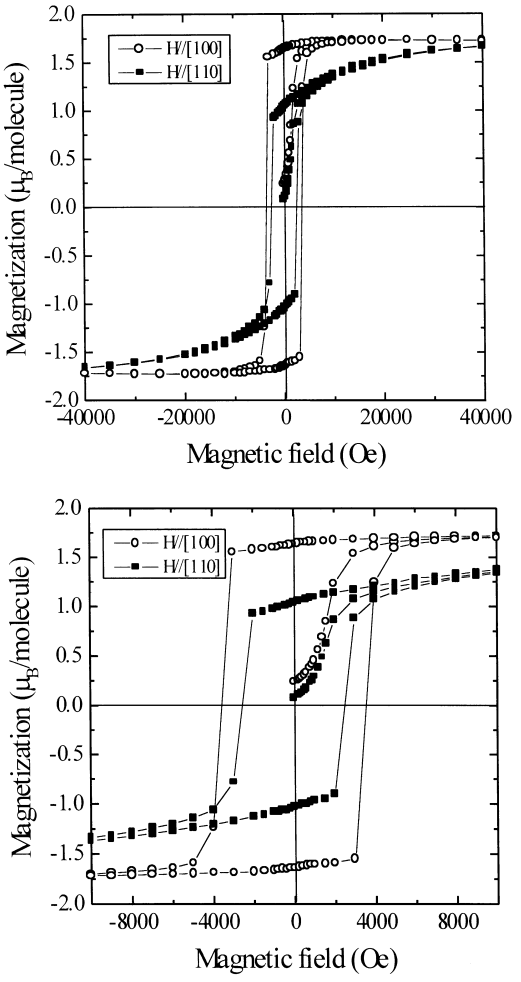


Fig. 2. The hysteresis curves of an $Mn_3O_4$ film with thickness 1.47 μm at 5 K. The magnetic field is applied along the [1 1 0] and [1 0 0] directions. (b) is an expansion of (a) to show the coercive force clearly.

been given [1–3] based on the triangular arrangement of the magnetic moments suggested by Yafet and Kittel [11]. Our work gives further evidence to support the triangular magnetic moment arrangements. However, the slightly smaller spontaneous magnetization and larger coercive force observed in the studied film than in the bulk single-crystal samples may be ascribed to the effects of the imperfect crystal structure of the film and the interface layer existing between the film and MgO substrate. This conjecture is verified by the results from a thinner

$Mn_3O_4$ film (980 nm), which gave a smaller spontaneous magnetization of 1.44 $\mu_B$/molecule and a large coercive force of about 4400 Oe for magnetization reversal under an applied field along [1 0 0]. So it is inferred that the thicker the film is, the larger its spontaneous magnetization is and the smaller its coercive force is for magnetization reversal. This conclusion has also been found in other thin epitaxial magnetic oxide films, such as $Fe_3O_4$(0 0 1) on MgO(0 0 1) by Margulies et al. [12,13], who suggested that antiphase boundaries play a key role in inducing anomalous magnetic behavior in single-crystal $Fe_3O_4$ films.

### 3.3. Dependence of magnetization on temperature

Fig. 3 shows the dependence of magnetization on temperature (5–100 K) at different magnetic fields and different cooling processes. In the case of zero-field-cooled (ZFC) condition, the sample was cooled from 300 to 5 K in the absence of an external magnetic field. Then a field ($H = 100, 10\,000$ and 20 000 Oe) was applied, and at the same time, the magnetization was measured as a function of temperature during the warming process. In the case of field-cooled (FC) process, the sample was cooled from 300 to 5 K in the presence of an external magnetic field. Then, the magnetization was measured as a function of temperature under this field during warming process. As seen in Fig. 3, a clear magnetic cooling effect is observed at low field magnetization. Since there is a strong magnetization anisotropy in the $Mn_3O_4$ crystal structure, the demagnetizing field in the film is so strong that the 100 Oe is not large enough to overcome its effect at low temperature. When the temperature is increasing close to the Curie temperature, the thermal agitation suppresses the demagnetizing field leading to an increase in magnetization. When the temperature is above the Curie temperature, ferrimagnetic long-range ordering disappears and magnetization drops sharply. So a magnetization cusp appears at the low-temperature side near the Curie temperature. Here, the derivative $|d(MT)/dT|$ maximum is used to determine the Curie temperature, where $M$ represents the magnetization intensity. It is found that the Curie temperature $T_{CF}$ is 46 K which is higher than the Curie temperature of

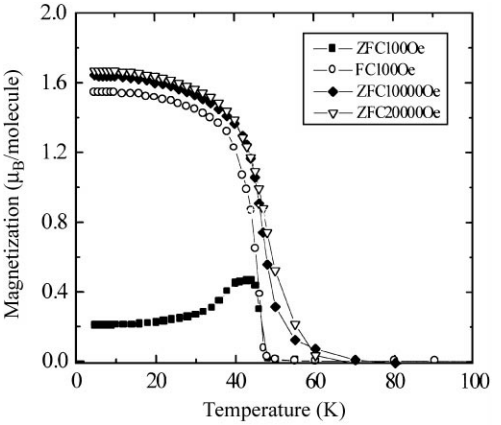


Fig. 3. Dependence of the magnetization on temperature for different magnetic fields 100, 10 000 and 20 000 Oe, applied along easy axis [1 0 0] under different cooling processes as marked in the figure. FC (or ZFC) expresses that the samples are being cooled from 300 to 5 K under (or without) applied fields.

bulk single-crystal samples, 42 K. The higher Curie temperature in the film can be attributed to the stronger exchange interactions between Mn ions, since the lattice parameter in the (0 0 1) plane of $Mn_3O_4$ films is 5.72 Å, a little smaller than its bulk lattice parameter which is 5.76 Å. For different $Mn_3O_4$ films, their Curie temperature is nearly the same. In Fig. 3, it is observed that the magnetization of the film is nearly saturated at a field of 10 000 Oe, which means that the higher field did not generate a clear increase in magnetization which is similar to the bulk sample owing to its inherent triangle moment arrangements [1,4].

The temperature dependence of the inverse magnetic susceptibility is shown in Fig. 4. The curve agrees well with the Curie–Weiss formula at temperatures higher than the Curie temperature. In the paramagnetic range, the magnetic susceptibility can be described as

$$\chi = \chi_0 + C/(T - T_{CF}) \quad (\text{emu/cm}^3\ \text{Oe}), \tag{1}$$

where $\chi_0 = 0.0067\,\text{emu/cm}^3\,\text{Oe}$, a temperature-independent susceptibility, $C = 0.102\,\text{emuK/cm}^3\,\text{Oe}$, an effective Curie constant, $T_{CF} = 46\,\text{K}$ the Curie temperature and $T$ the absolute temperature. In expressing the magnetic susceptibility in the paramagnetic range as a function of average effective

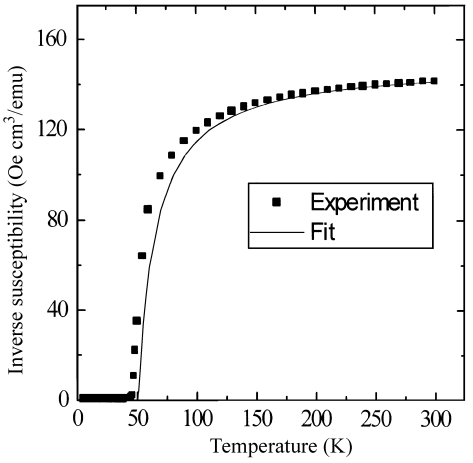


Fig. 4. Temperature dependence of the inverse susceptibility in the paramagnetic range.

moment of each Mn ion, the Curie–Weiss law in the general form is written as: $\chi = \chi_0 + N\mu_{\text{eff}}^2/3k_B(T - T_{CF})$, where $N$ is the number density of Mn ions, $\mu_{\text{eff}}$ the effective magnetic moment of each Mn ion, $k_B$ the Boltzmann constant. Using Eq. (1), we obtained $\mu_{\text{eff}} = 3.59\,\mu_B$/molecule, which is far smaller than the moment $5.24\,\mu_B$/molecule calculated with the ionic formula $Mn^{2+}Mn_2^{3+}O_4^{2-}$ and considering the contribution of electronic spins only [3]. A smaller effective moment may originate due to the same reasons as the smaller spontaneous magnetization from the films.

## 4. Conclusions

Plasma-assisted MBE has been used to grow single-crystal $Mn_3O_4$ thin films. Their structural and magnetic properties have been studied. Although the magnetic properties of the films are basically similar to bulk $Mn_3O_4$ single-crystal samples, some different features show up due to the effects of distortion of structure parameters, the interface layer between the film and substrate and the structural defects. It is found that the Curie temperature of the $Mn_3O_4$ film grown on the MgO substrate is higher than that of bulk single-crystal samples due to decreasing of atomic distances and enhancing the exchange interactions of Mn atoms. The films exhibit magnetization anisotropy in the growing plane, the difference of coercive forces between the [1 1 0] and [1 0 0] axes is about 1000 Oe, which is nearly independent of the film thickness. The spontaneous magnetization is $1.73\,\mu_B$/molecule which lies in between the values of $1.56\,\mu_B$/molecule for polycrystalline and $1.85\,\mu_B$/molecule for bulk single-crystal samples. It is found that the interface has a greater influence on the spontaneous magnetization and the coercive force for thinner films. The temperature dependence of the inverse magnetic susceptibility in the paramagnetic range agrees well with the Curie–Weiss formula.

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